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Engineering models for synthetic microvascular materials with interphase mass, momentum and energy transfer

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ABSTRACT

New materials are being developed that consist of a solid matrix with pores or vessels through which a functional fluid phase may pass. The fluid can provide expanded functionality such as healing and remodeling, damage disclosure, enhanced heat transfer, and controlled deformation, stiffness and damping. This paper presents a class of engineering models for synthetic microvascular materials that have fluid passages much smaller than a characteristic structural length such as panel thickness. The materials are idealized as two-phase continua with a solid phase and a fluid phase occupying every volume. The model permits the solid and fluid phases to exchange mass, momentum and energy. Balance equations and the entropy inequality for general mixtures are taken from existing continuum mixture theory. These are augmented with certain definite types of solid–fluid interactions in order to enable adequately general, but workable, engineering analysis. The thermomechanical characteristics of this restricted class of materials are delineated. By demanding that the law of increase of entropy be satisfied for all processes, much is deduced about the acceptable forms of constitutive equations and internal state variable evolution equations. The paper concludes with a study of the uniaxial tension behavior of an idealized vascular material.

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1. Introduction

Biological tissues incorporate vessels that transport blood, sap and other fluids to assist with healing and remodeling, thermal regulation and other vital functions. With these naturally occurring examples in mind, researchers have envisioned, and in some cases fabricated, synthetic materials intended to expand the functionality and robustness of structures in critical applications. Artificial tissues for biomedical applications, as well as aerospace structures required to endure highly variable loads and heat fluxes while minimizing weight, could benefit greatly from the development of practical synthetic vascular materials. To create and apply such materials, quantitative simulation will be necessary.

The goal of this work is a rigorous but practicable continuum model of a material in which a solid and a fluid phase can exchange mass, momentum and energy. Such a model would enable analysis and simulation of synthetic materials with expanded functionality. Self-healing, for example, involves mass transfer from a fluid phase to a solid phase. White et al. (2001) demonstrated an early self-healing material that incorporated healing resins in microcapsules that release their contents when a macroscopic crack occurs. Toohey et al. (2007) discussed a material with continuous passages

such that resin could eventually be transported as needed to the healing site. Hager et al. (2010) and van der Zwaag et al. (2007) reviewed several years of work on self-healing materials, including polymers healed by resins released in response to damage. These reviews reveal much progress on the physical chemistry of healing, but only limited modeling, which tends to be *ad hoc* and focused on the healing process itself, not the overall mechanics. Schimmel and Remmers (2006) developed a constitutive model for self-healing composites, but it was limited to one dimension and only applied to a specific damage and healing scenario.

A material in which heat can be transported from or to a load-bearing solid skeleton by a flowing fluid opens the door to autonomous thermal regulation. To model such processes, the solid and fluid must be able to exchange energy. For high-temperature aerospace applications, Rakow and Waas (2007) proposed running coolant through structural open-celled metal foams. This built on earlier work in actively cooled structures, such as the fluid-cooled wing leading edge of Pinckney et al. (1975). Modeling of these structures has hitherto involved separate thermal and mechanical models.

Transport of fluid must involve a mechanical interaction between the solid and fluid. A fluid exerts a drag force on any solid body it washes. Therefore, a complete model must also account for momentum transfer between the solid and fluid. The force exerted on the solid by the fluid could also be exploited to control the volume or shape of the material.

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With unlimited resources, it is possible to model nearly anything as a collection of discrete components. However, for materials in which the passages are very small relative to other features of interest, and in which thermal and mechanical phenomena are tightly coupled, there are distinct practical advantages in a single, continuous thermomechanical material model. Not least among these is ready compatibility with existing finite element methods. Modeling of materials in which several constituents or phases are combined is in the domain of continuum mixture theory as laid out by Truesdell and Toupin (1960) and elaborated by such subsequent workers as Bedford and Drumheller (1983). Classical mixture theory accounts for the three interphase interactions (mass, momentum and energy) we wish to model.

Much work has been done in applying mixture theory to living materials. Klisch et al. (2003) developed an isothermal, incompressible model of articular cartilage that incorporated both mass and momentum transfer. Tao et al. (2001) used mixture theory to isothermally model the transport of water in incompressible soft tissue. Garikipati et al. (2004) presented a model accounting for growth in biological tissue that included multiple reacting chemical constituents but was limited to mixtures in which all constituents have the same temperature. Humphrey and Rajagopal (2002) presented a very general constrained mixture model for biological tissues that included growth. Growth, that is, taking up material from the surroundings, is a characteristic of living material that is not considered for the synthetic materials addressed by the present work.

Living materials contain several solid and fluid constituents. These constituents can interact chemically, biologically and electromagnetically, as well as thermomechanically, in ways that are not completely understood. The difficulty of attempting to account for all these aspects is usually mitigated by imposing assumptions such as incompressibility and the isothermal assumption that would limit the potential of synthetic materials.

Mixture theory has also been employed to model synthetic materials, although not the vascular materials we consider here. Rajagopal et al. (1994) modeled isothermal flows of electrorheological materials, which are essentially suspensions. Krishnan and Rao (2001); Wang et al. (2004) and others have used mixture theory to model asphalt and concrete.

1.1. Approach

In addition to its practical aims, this work will attempt to bring clarity to the theoretical treatment of interphase mass, momentum and energy transfer. Both the practical and theoretical aims of this work require the level of generality to be chosen judiciously.

We limit the treatment to one solid and one fluid phase. Each phase could consist of more than one constituent; for example, some of the passages in a self-healing material may contain resin and some may contain hardener. For a material with a skeleton composed of several solid constituents, the solids could be homogenized into an effective solid phase. The same is intended for the fluid. The term *interphase* is used here to describe interactions between the solid and fluid phases.

Mass, momentum and energy are assumed to be supplied by one phase to the other according to simple terms in the balance laws, but the constitutive equations for these interactions need only satisfy the law of increase of entropy. Growth in the sense of volumetric takeup of mass from the surroundings (e.g., Loret and Simões (2005)) is excluded. There does not need to be any *a priori* kinematic constraint between the fluid and solid, although it will be shown how to define one if desired.

The density of fluid or solid in any volume can become insignificantly small, but cannot totally vanish without violating continuity. Cracks, shocks, material boundaries and other discontinuities

must be handled through jump conditions that are outside the scope of this paper.

By definition, a continuum mixture theory spatially averages out the microstructural details. However, constitutive equations can certainly be microstructurally motivated. Constitutive laws for specific materials can account for solid and fluid intrinsic characteristics, passage geometry, interphase thermal interactions, etc. This is analogous to treating a composite lamina as a transversely isotropic continuum but building its properties up from the properties of the fibers and matrix.

2. Kinematics

The material consists of a solid phase with motion $\mathbf{x}_s = \mathbf{X}_s(X_s, t)$ and a fluid phase with motion $\mathbf{x}_f = \mathbf{X}_f(X_f, t)$, where X is the label of a specific particle. The motions permit the presence of both fluid and solid at the same location. Quantities subscripted “s” are associated with the solid phase and those subscripted “f” are associated with the fluid phase. When an equation takes the same form for both the solid and the fluid, it may be written with subscript “a” rather than repeating it for both phases. The density of the material is the sum of the partial densities of the phases:

$$\rho = \rho_s + \rho_f \quad (1)$$

and the phase mass concentrations are defined to be

$$c_a \equiv \rho_a / \rho. \quad (2)$$

The velocities of the phases are $\mathbf{v}_a \equiv \partial \mathbf{x}_a / \partial t$. The velocity of each phase is referred to the density-weighted mean velocity

$$\mathbf{v} \equiv c_s \mathbf{v}_s + c_f \mathbf{v}_f. \quad (3)$$

The diffusion velocities are the differences between the absolute velocities and the mean velocity:

$$\mathbf{u}_a \equiv \mathbf{v}_a - \mathbf{v}. \quad (4)$$

The excess velocity of the fluid with respect to the solid is

$$\mathbf{w} \equiv \mathbf{v}_f - \mathbf{v}_s = \mathbf{u}_f - \mathbf{u}_s. \quad (5)$$

By Eqs. (1), (3) and (4),

$$\rho_s \mathbf{u}_s + \rho_f \mathbf{u}_f = \mathbf{0}. \quad (6)$$

The superposed filled circle (\bullet), empty circle (\circ) and dot ($\dot{}$) denote the following material derivatives of any field quantity ϕ :

$$\dot{\phi} \equiv \phi' + (\text{grad } \phi) \mathbf{v}_s \quad \text{for matter moving with solid velocity,} \quad (7)$$

$$\circ \phi \equiv \phi' + (\text{grad } \phi) \mathbf{v}_f \quad \text{for matter moving with the fluid velocity,} \quad (8)$$

$$\dot{\phi} \equiv \phi' + (\text{grad } \phi) \mathbf{v} \quad \text{for matter moving with the mean velocity,} \quad (9)$$

where $'$ means $\partial / \partial t$. From the foregoing,

$$\dot{\phi} \equiv \dot{\phi} + (\text{grad } \phi) \mathbf{u}_s \quad (10)$$

$$\dot{\phi} \equiv \dot{\phi} + (\text{grad } \phi) \mathbf{u}_f = \dot{\phi} + (\text{grad } \phi) \mathbf{w} \quad (11)$$

An identity relating the material derivative for mean-velocity matter ($\dot{}$) to the phase material derivatives (\bullet and \circ) was presented by Truesdell and Toupin (1960). In terms of the solid and fluid quantities defined here, it is

$$\begin{aligned} \rho \dot{\phi} &= \rho_s \dot{\phi}_s + [\rho'_s + \text{div}(\rho_s \mathbf{v}_s)] \phi_s - \text{div}(\rho_s \phi_s \mathbf{u}_s) \\ &\quad + \rho_f \circ \phi_f + [\rho'_f + \text{div}(\rho_f \mathbf{v}_f)] \phi_f - \text{div}(\rho_f \phi_f \mathbf{u}_f) \\ &\quad - [\rho' + \text{div}(\rho \mathbf{v})] \phi, \end{aligned} \quad (12)$$

where $\phi \equiv c_s \phi_s + c_f \phi_f$. By setting $\phi_s = \phi_f = 1$ and using (6), we obtain the *purely kinematic* result

$$\dot{\rho} + \rho \text{div } \mathbf{v} = \dot{\rho}_s + \rho_s \text{div } \mathbf{v}_s + \dot{\rho}_f + \rho_f \text{div } \mathbf{v}_f. \quad (13)$$

3. Balance laws

In this section, phase interactions of specific forms are introduced; to make clear what is being asserted, these must be fit into an existing theory of mixtures. The balance laws and thermodynamics of mixtures have been treated by many authors. Gurtin and Vargas (1971) placed the pre-1960 theory of fluid mixtures within the context of continuum thermodynamics and proved several claims that previously were only postulated, while Gurtin (1971) used thermodynamic arguments to deduce further properties of the interactions in reacting inviscid fluid mixtures. Here, we start with the formulation of Bowen (1976), which recapitulated the 1965–1975 theoretical developments for a mixture exchanging mass, momentum and energy, and simplify to two phases.

3.1. Mass balance

Bowen's formulation lays down formal balance laws for the mixture as a whole and for the phases, and then states the conditions that must hold in order for the mixture and phase laws to be consistent. There remains only to give definite forms to the phase supply terms in the balance laws.

The mean quantities for the vascular material are postulated to satisfy the single-phase mass balance

$$\dot{\rho} + \rho \operatorname{div} \mathbf{v} = 0. \quad (14)$$

Using identity (13), it can be seen that the phase mass balances

$$\dot{\rho}_s + \rho_s \operatorname{div} \mathbf{v}_s = \hat{\rho} \quad (15)$$

$$\dot{\rho}_f + \rho_f \operatorname{div} \mathbf{v}_f = -\hat{\rho}, \quad (16)$$

are consistent with the material mass balance (14). In (15) and (16), $\hat{\rho}$ is the interphase mass transfer.

3.2. Linear momentum balance

The Cauchy stress in the vascular material, in terms of phase quantities, is

$$\mathbf{T} \equiv \mathbf{T}_s + \mathbf{T}_f - \rho_s \mathbf{u}_s \otimes \mathbf{u}_s - \rho_f \mathbf{u}_f \otimes \mathbf{u}_f. \quad (17)$$

With this definition and a mean body force defined as $\mathbf{b} \equiv c_s \mathbf{b}_s + c_f \mathbf{b}_f$, the vascular material is postulated to satisfy

$$\rho \dot{\mathbf{v}} = \operatorname{div} \mathbf{T} + \rho \mathbf{b}. \quad (18)$$

Bowen (1976) postulates that the phases satisfy analogous laws with momentum supplies $\hat{\mathbf{p}}_s$ and $\hat{\mathbf{p}}_f$:

$$\rho_s \dot{\mathbf{v}}_s = \operatorname{div} \mathbf{T}_s + \rho_s \mathbf{b}_s + \hat{\mathbf{p}}_s, \quad \rho_f \dot{\mathbf{v}}_f = \operatorname{div} \mathbf{T}_f + \rho_f \mathbf{b}_f + \hat{\mathbf{p}}_f; \quad (19)$$

the momentum supplies must satisfy

$$\hat{\mathbf{p}}_s + \hat{\mathbf{p}}_f + \hat{\rho}(\mathbf{u}_s - \mathbf{u}_f) = \mathbf{0}. \quad (20)$$

in order to render (19) consistent with (18). This requirement can be satisfied by many choices of $\hat{\mathbf{p}}_s$ and $\hat{\mathbf{p}}_f$; we choose

$$\hat{\mathbf{p}}_s \equiv \mathbf{f} + \hat{\rho} \mathbf{u}_f \quad (21)$$

$$\hat{\mathbf{p}}_f \equiv -\mathbf{f} - \hat{\rho} \mathbf{u}_s, \quad (22)$$

where \mathbf{f} is the interphase momentum transfer. This choice may appear expedient, but it amounts to a formalism; it merely segregates the constitutive part \mathbf{f} of the volumetric force from the part due to mass transfer. Then the phase momentum balances become

$$\rho_s \dot{\mathbf{v}}_s = \operatorname{div} \mathbf{T}_s + \rho_s \mathbf{b}_s + \mathbf{f} + \hat{\rho} \mathbf{u}_f \quad (23)$$

$$\rho_f \dot{\mathbf{v}}_f = \operatorname{div} \mathbf{T}_f + \rho_f \mathbf{b}_f - \mathbf{f} - \hat{\rho} \mathbf{u}_s. \quad (24)$$

Physically, a healing or remodeling process involves fluid gradually solidifying by a chemical or physical change that takes a finite

amount of time to occur. Solidifying fluid could be regarded as a third phase with a velocity that transitions continuously from the fluid velocity to the solid velocity as the solidification proceeds. But in the present theory, there are only two phases, so a phase change necessarily involves transition through an intermediate state not “seen” by the theory. An instantaneous change from the fluid to the solid velocity would require an infinite force, which we assert is unacceptable. Equivalently, we exclude interactions where momentum transfer during the phase change is significant. We therefore stipulate that

$$\hat{\rho}(\mathbf{u}_f - \mathbf{u}_s) = \hat{\rho} \mathbf{w} = \mathbf{0}. \quad (25)$$

That is, interphase mass transfer can only occur when and where the fluid and solid are at rest relative to one another. Although we leave the momentum balances in the forms (23) and (24), with differing fluid and solid velocities, requirement (25) means that any transferred mass must in fact leave the fluid and enter the solid with the same velocity.

3.3. Angular momentum balance

The balance of angular momentum for a single-phase continuum with no body couples or couple-stresses is

$$\mathbf{T} = \mathbf{T}^T. \quad (26)$$

We assume that the phases themselves sustain no body couples or couple-stresses, exchanging angular momentum only as the moment of the exchanged linear momentum. Under these assumptions,

$$\mathbf{T}_a = \mathbf{T}_a^T \quad (27)$$

Given that $\mathbf{u}_a \otimes \mathbf{u}_a$ in (17) are symmetric, Eq. (26) is trivially satisfied.

3.4. Energy balance

The heat flux vector, internal energy and volumetric heat supply in the vascular material are defined in terms of phase quantities as

$$\mathbf{q} \equiv \mathbf{q}_s + \mathbf{q}_f - \mathbf{T}_s^T \mathbf{u}_s - \mathbf{T}_f^T \mathbf{u}_f + \rho_s \mathbf{u}_s \left(\varepsilon_s + \frac{\mathbf{u}_s \cdot \mathbf{u}_s}{2} \right) + \rho_f \mathbf{u}_f \left(\varepsilon_f + \frac{\mathbf{u}_f \cdot \mathbf{u}_f}{2} \right) \quad (28)$$

$$\varepsilon \equiv c_s \left(\varepsilon_s + \frac{\mathbf{u}_s \cdot \mathbf{u}_s}{2} \right) + c_f \left(\varepsilon_f + \frac{\mathbf{u}_f \cdot \mathbf{u}_f}{2} \right) \quad (29)$$

$$r \equiv c_s r_s + c_f r_f. \quad (30)$$

With these definitions, it is postulated that the vascular material satisfies

$$\rho \dot{\varepsilon} = \mathbf{T} \cdot \mathbf{L} - \operatorname{div} \mathbf{q} + \rho r + \rho_s \mathbf{u}_s \cdot \mathbf{b}_s + \rho_f \mathbf{u}_f \cdot \mathbf{b}_f, \quad (31)$$

which is the same as the energy balance for a single-phase medium except for the last two terms, which represent work done by the body forces against the diffusive motions of the phases. In (31), $\mathbf{L} \equiv \operatorname{grad} \mathbf{v}$ is the velocity gradient and r is an externally supplied heat rate per unit volume. The phases are assumed to satisfy the classical laws with the addition of supply terms $\hat{\varepsilon}$:

$$\rho_s \dot{\varepsilon}_s = \mathbf{T}_s \cdot \mathbf{L}_s - \operatorname{div} \mathbf{q}_s + \rho_s r_s + \hat{\varepsilon}_s \quad (32)$$

$$\rho_f \dot{\varepsilon}_f = \mathbf{T}_f \cdot \mathbf{L}_f - \operatorname{div} \mathbf{q}_f + \rho_f r_f + \hat{\varepsilon}_f. \quad (33)$$

For Eqs. (31)–(33) to be consistent, the phase heat supplies $\hat{\varepsilon}_s$ and $\hat{\varepsilon}_f$ must satisfy

$$\hat{\varepsilon}_s + \hat{\varepsilon}_f + \mathbf{u}_s \cdot \hat{\mathbf{p}}_s + \mathbf{u}_f \cdot \hat{\mathbf{p}}_f + \hat{\rho} \left(\varepsilon_s - \varepsilon_f + \frac{\mathbf{u}_s \cdot \mathbf{u}_s - \mathbf{u}_f \cdot \mathbf{u}_f}{2} \right) = 0. \quad (34)$$

By Eqs. (5), (21), (22) and (25), requirement (34) reduces to

$$\hat{\varepsilon}_s + \hat{\varepsilon}_f = \mathbf{w} \cdot \mathbf{f} + \hat{\rho}(\varepsilon_f - \varepsilon_s). \quad (35)$$

An obvious, but by no means unique, choice of $\hat{\varepsilon}_s$ and $\hat{\varepsilon}_f$ that satisfies (35) is

$$\hat{\varepsilon}_s \equiv z + \frac{\mathbf{w} \cdot \mathbf{f}}{2} + \hat{\rho} \varepsilon_f \quad (36)$$

$$\hat{\varepsilon}_f \equiv -z + \frac{\mathbf{w} \cdot \mathbf{f}}{2} - \hat{\rho} \varepsilon_s. \quad (37)$$

Like choices (21) and (22), this is merely a formalism that segregates the constitutive part z (which at this point can take arbitrary form) of the interphase heat transfer rate from other contributors. In these equations, $\mathbf{w} \cdot \mathbf{f}$ is the rate of work per unit volume done by the interphase force, and z is the rate of interphase heat transfer per unit volume.

With choices (36) and (37), the energy balances for the phases are

$$\rho_s \dot{\varepsilon}_s = \mathbf{T}_s \cdot \mathbf{L}_s - \text{div} \mathbf{q}_s + \rho_s r_s + z + \frac{\mathbf{w} \cdot \mathbf{f}}{2} + \hat{\rho} \varepsilon_f \quad (38)$$

$$\rho_f \dot{\varepsilon}_f = \mathbf{T}_f \cdot \mathbf{L}_f - \text{div} \mathbf{q}_f + \rho_f r_f - z + \frac{\mathbf{w} \cdot \mathbf{f}}{2} - \hat{\rho} \varepsilon_s. \quad (39)$$

The above two equations involve the internal energy, but subsequent developments require the concepts of entropy and temperature. These are introduced through the definition

$$\Lambda_a \equiv \rho_a (\eta_a - \vartheta_a \varepsilon_a) \quad (40)$$

where the existence of specific entropies η_a is asserted, Λ_a are the *Massieu potentials* (per unit present volume), and ϑ_a are the *coldnesses* (reciprocals of the absolute temperatures θ_a). We postpone writing the entropy forms of the energy equations until a relation between η_a and Λ_a is obtained.

4. Entropy axiom

For single-phase materials, the Clausius–Duhem statement of the law of entropy increase is used. Bowen and Garcia (1970) generalized the Clausius–Duhem inequality for mixtures of n phases with distinct temperatures, distinct velocities and mass exchange between the phases. They then used this axiom to investigate constitutive equations for phases that did not exchange mass. Subsequently, Bowen (1979) investigated constitutive equations for phases that could exchange mass but not momentum.

We wish to preserve distinct temperatures and velocities (to allow heat removal by the fluid) as well as mass exchange (to allow healing). Therefore, we use the axiom of Bowen and Garcia (1970) in its full generality. However, we limit the analysis to two phases and make some assumptions as to the constitutive responses of the phases.

The entropy axiom, specialized to our two-phase mixture with the phase supply terms chosen in Section 3, is

$$\begin{aligned} \dot{\Lambda}_s + \dot{\Lambda}_f + \rho_s \left(\frac{\eta_s}{\vartheta_s} - \frac{\Lambda_s}{\rho_s \vartheta_s} \right) \dot{\vartheta}_s + \rho_f \left(\frac{\eta_f}{\vartheta_f} - \frac{\Lambda_f}{\rho_f \vartheta_f} \right) \dot{\vartheta}_f + \text{tr}[(\Lambda_s \mathbf{I} + \vartheta_s \mathbf{T}_s^T) \mathbf{L}_s] \\ + \text{tr}[(\Lambda_f \mathbf{I} + \vartheta_f \mathbf{T}_f^T) \mathbf{L}_f] + \mathbf{q}_s \cdot \mathbf{s}_s + \mathbf{q}_f \cdot \mathbf{s}_f + \vartheta_s \left(\frac{\mathbf{w} \cdot \mathbf{f}}{2} + z \right) \\ + \vartheta_f \left(\frac{\mathbf{w} \cdot \mathbf{f}}{2} - z \right) \geq 0, \end{aligned} \quad (41)$$

where $\mathbf{s}_a \equiv \text{grad } \vartheta_a$ are the *coldness gradients*. The quantities $\Lambda_a \mathbf{I} + \vartheta_a \mathbf{T}_a^T$ play a role similar to that of the (scalar) chemical potentials of classical thermodynamics, and may be written as $-\rho_a \mathbf{K}_a \vartheta_a$, where \mathbf{K}_a are generalized chemical potentials (Bowen, 1976).

5. Constitutive equations

5.1. Processes and physical variables

Balance laws (15), (16), (23), (24), (38) and (39) are one vector equation and two scalar equations for each phase. The dependent variables $\mathbf{T}_a, \mathbf{q}_a, \Lambda_a, \eta_a, \hat{\rho}, \mathbf{f}$ and z require constitutive equations. The independent variables are the motions \mathcal{X}_a and the coldnesses ϑ_a . The balancing variables \mathbf{b}_a, ρ_a and r_a may take on such values as to satisfy the balance laws no matter the values of the other variables, so that arbitrary hypothetical processes consisting of *specified histories of motion and coldness in both phases* are assured to exist. These processes determine any kinematic quantities such as the velocities \mathbf{v}_a and the excess velocity \mathbf{w} , as well as the coldness gradients.

5.2. Internal state variables

Internal state variables are a conventional way to define internal material states such as damage that can then be made available as dependent variables in constitutive equations. Internal variables do not directly appear in the balance laws but rather are governed by evolution equations. One may append internal variables to the theory provided one also postulates evolution equations for them.

Because volume fractions are so often of interest, we define the fluid volume fraction as a standard internal variable ζ , and denote the tuple (not a vector) of any other “auxiliary” internal variables as α . As we shall see, it is possible to solve some problems without considering volume fractions, but a volume fraction is always available if needed. A mixture for which the volume fractions do not affect the behavior is generally called *miscible* (Bedford and Drumheller, 1983).

The fluid volume fraction allows us to distinguish the distribution of matter in the two arbitrarily small parcels of material shown in Fig. 1, which both have the same solid and fluid densities. Interpreting the fluid volume fraction as the present volume of fluid per present total volume, the intrinsic densities are related to the partial densities by

$$\rho_f = \zeta \bar{\rho}_f, \quad \rho_s = (1 - \zeta) \bar{\rho}_s, \quad (42)$$

where the bar indicates the intrinsic density. This assumes the fluid saturates the solid.

When there is no motion ($\mathbf{v}_s = \mathbf{0}$ and $\mathbf{v}_f = \mathbf{0}$), Eqs. (15), (16) and (42) reduce to

$$-\zeta' \bar{\rho}_f + (1 - \zeta) \bar{\rho}_s' = \hat{\rho} \quad (43)$$

$$\zeta' \bar{\rho}_f + \zeta \bar{\rho}_f' = -\hat{\rho}, \quad (44)$$

implying that one of $\zeta, \bar{\rho}_s, \bar{\rho}_f$ is no longer independent. If the phases are intrinsically incompressible ($\bar{\rho}_a' = 0$) and of different intrinsic densities, the above equations can be satisfied only if $\zeta' = 0$ and $\hat{\rho} = 0$. That is, when intrinsically incompressible fluid is converted to intrinsically incompressible solid with a different density, there must be a motion, which is the swelling or shrinkage intuitively expected. Eq. (25) implies that during such swelling/shrinkage, the

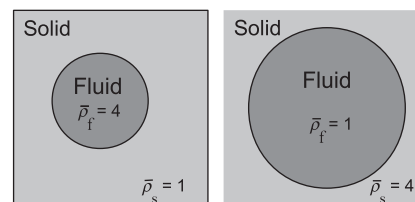


Fig. 1. Two parcels of material with the same fluid and solid densities but different fluid volume fractions.

solid and fluid can have no *relative* motion, as would be the case regardless of their intrinsic compressibility.

Additional internal state variables, collected in the tuple α , may be used for tracking relaxation, damage and healing. These may include scalars α_i , vectors \mathbf{a}_i and tensors \mathbf{A}_i .

5.3. Constitutive assumptions

It is assumed that each phase obeys the principle of equipresence (Truesdell and Noll, 2004), but that the material as a whole does not, because the underlying molecular motions are different in fluids and solids. Bedford and Drumheller (1983) call this the *principle of phase separation*, and in other contexts mixtures satisfying this principle are called *ideal mixtures*. (Bowen, 1976) The principle of phase separation would be inapplicable for mixtures of more than one fluid because it would lead to contradictions of certain principles of thermochemistry (Bowen, 1969).

5.4. Second-law reduction of constitutive equations

The functional forms for the constitutive equations, consistent with the assumptions given in the previous section, are

Stress in the solid	$\mathbf{T}_s(\mathbf{F}_s, \rho_s, \vartheta_s, \mathbf{s}_s, \zeta, \alpha)$
Heat flux vector in the solid	$\mathbf{q}_s(\mathbf{F}_s, \rho_s, \vartheta_s, \mathbf{s}_s, \zeta, \alpha)$
Massieu potential per unit volume in the solid	$\Lambda_s(\mathbf{F}_s, \rho_s, \vartheta_s, \mathbf{s}_s, \zeta, \alpha)$
Specific entropy in the solid	$\eta_s(\mathbf{F}_s, \rho_s, \vartheta_s, \mathbf{s}_s, \zeta, \alpha)$
Stress in the fluid	$\mathbf{T}_f(\rho_f, \mathbf{D}_f, \vartheta_f, \mathbf{s}_f, \zeta, \alpha)$
Heat flux vector in the fluid	$\mathbf{q}_f(\rho_f, \mathbf{D}_f, \vartheta_f, \mathbf{s}_f, \zeta, \alpha)$
Massieu potential per unit volume in the fluid	$\Lambda_f(\rho_f, \mathbf{D}_f, \vartheta_f, \mathbf{s}_f, \zeta, \alpha)$
Specific entropy in the fluid	$\eta_f(\rho_f, \mathbf{D}_f, \vartheta_f, \mathbf{s}_f, \zeta, \alpha)$
Interphase mass transfer	$\hat{\rho}(\mathbf{F}_s, \mathbf{D}_f, \mathbf{w}, \vartheta_s, \vartheta_f, \rho_s, \rho_f, \zeta, \alpha)$
Interphase force	$\mathbf{f}(\mathbf{F}_s, \mathbf{D}_f, \mathbf{w}, \vartheta_s, \vartheta_f, \rho_s, \rho_f, \zeta, \alpha)$
Interphase heat transfer	$z(\mathbf{F}_s, \mathbf{D}_f, \mathbf{w}, \vartheta_s, \vartheta_f, \rho_s, \rho_f, \zeta, \alpha)$

In the functions above, $\mathbf{D}_f \equiv \frac{1}{2}(\mathbf{L}_f^T + \mathbf{L}_f)$ is the symmetric part of the velocity gradient.

For materials that have no interphase mass transfer ($\hat{\rho} = 0$), balance of mass leads to the familiar identity

$$\rho_a = \rho_{aR} / \det \mathbf{F}_a. \quad (45)$$

In such cases, it is not necessary to include ρ_a in an argument list that already includes \mathbf{F}_a . But if $\hat{\rho} \neq 0$, (45) does not hold and ρ_a depends in general on both \mathbf{F}_a and $\hat{\rho}$. Therefore, we explicitly include ρ_s in the solid argument lists. In a theory of mixtures with interphase mass exchange, Bowen (1969) included it in the combination $\rho_a \det \mathbf{F}_a$, and in a more recent investigation Ambrosi et al. (2010) showed that such dependence leads naturally to stresses associated solely with interphase mass exchange.

The interphase mass transfer considered here is a special case of a density change driven by causes other than deformation. Different approaches observed in the literature include special reference configurations in which ρ_{aR} already accounts for the present level of mass transfer, analogous to subtracting the “thermal strain” from a body that has undergone thermal expansion, and various decompositions of the deformation gradient. Comparison of the present approach to existing approaches is outside the scope of this paper.

While these argument lists are lengthy, they do not aim for maximum generality. For example, in mixtures of fluids, it is necessary to include a dependence on the second gradient of deformation (which implies a dependence on the density gradient), or else a buoyancy-like force known to exist in a mixture of isothermal

fluids at rest will fail to be predicted. That effect is not relevant here, so the second gradient of deformation is not included in these argument lists.

Substituting the proposed functional forms into inequality (41), we obtain

$$\begin{aligned} & \left[\frac{\partial \Lambda_s}{\partial \mathbf{F}_s} \mathbf{F}_s^T + \left(\Lambda_s - \frac{\partial \Lambda_s}{\partial \rho_s} \rho_s \right) \mathbf{I} + \vartheta_s \mathbf{T}_s \right] \cdot \mathbf{L}_s + \left(\frac{\partial \Lambda_s}{\partial \rho_s} - \frac{\partial \Lambda_f}{\partial \rho_f} \right) \hat{\rho} \\ & + \left[\left(\Lambda_f - \frac{\partial \Lambda_f}{\partial \rho_f} \rho_f \right) \mathbf{I} + \vartheta_f \mathbf{T}_f \right] \cdot \mathbf{D}_f + \left[\frac{\partial \Lambda_s}{\partial \vartheta_s} + \rho_s \left(\frac{\eta_s}{\vartheta_s} - \frac{\Lambda_s}{\rho_s \vartheta_s} \right) \right] \dot{\vartheta}_s \\ & + \left[\frac{\partial \Lambda_f}{\partial \vartheta_f} + \rho_f \left(\frac{\eta_f}{\vartheta_f} - \frac{\Lambda_f}{\rho_f \vartheta_f} \right) \right] \dot{\vartheta}_f + \frac{\partial \Lambda_s}{\partial \mathbf{s}_s} \cdot \dot{\mathbf{s}}_s + \frac{\partial \Lambda_s}{\partial \zeta} \dot{\zeta} + \frac{\partial \Lambda_s}{\partial \alpha} \cdot \dot{\alpha} \\ & + \frac{\partial \Lambda_f}{\partial \mathbf{D}_f} \cdot \dot{\mathbf{D}}_f + \frac{\partial \Lambda_f}{\partial \mathbf{s}_f} \cdot \dot{\mathbf{s}}_f + \frac{\partial \Lambda_f}{\partial \zeta} \dot{\zeta} + \frac{\partial \Lambda_f}{\partial \alpha} \cdot \dot{\alpha} + \mathbf{q}_s \cdot \mathbf{s}_s + \mathbf{q}_f \cdot \mathbf{s}_f \\ & + z(\vartheta_s - \vartheta_f) + \frac{\vartheta_s + \vartheta_f}{2} \mathbf{w} \cdot \mathbf{f} \geq 0 \end{aligned} \quad (46)$$

where the chain rule, Eqs. (15) and (16), and $\dot{\mathbf{F}}_s = \mathbf{L}_s \mathbf{F}_s$ have been used. In dot products involving the tuple α of internal variables, the dot is to be interpreted as scalar multiplication for scalars α_i , the vector inner product for vectors \mathbf{a}_i and the tensor inner product for tensors \mathbf{A}_i .

We now apply the well-known procedure of Coleman and Noll (1963) to deduce that several terms in inequality (46) must be zero. First, we segregate some terms into a separate inequality:

$$\begin{aligned} & \left(\frac{\partial \Lambda_s}{\partial \rho_s} - \frac{\partial \Lambda_f}{\partial \rho_f} \right) \hat{\rho} + \frac{\partial \Lambda_s}{\partial \zeta} \dot{\zeta} + \frac{\partial \Lambda_s}{\partial \alpha} \cdot \dot{\alpha} + \frac{\partial \Lambda_f}{\partial \zeta} \dot{\zeta} + \frac{\partial \Lambda_f}{\partial \alpha} \cdot \dot{\alpha} + \mathbf{q}_s \cdot \mathbf{s}_s + \mathbf{q}_f \cdot \mathbf{s}_f \\ & + z(\vartheta_s - \vartheta_f) + \frac{\vartheta_s + \vartheta_f}{2} \mathbf{w} \cdot \mathbf{f} \geq 0. \end{aligned} \quad (47)$$

Remaining is

$$\begin{aligned} & \left[\frac{\partial \Lambda_s}{\partial \mathbf{F}_s} \mathbf{F}_s^T + \left(\Lambda_s - \frac{\partial \Lambda_s}{\partial \rho_s} \rho_s \right) \mathbf{I} + \vartheta_s \mathbf{T}_s \right] \cdot \mathbf{L}_s + \left[\left(\Lambda_f - \frac{\partial \Lambda_f}{\partial \rho_f} \rho_f \right) \mathbf{I} + \vartheta_f \mathbf{T}_f \right] \cdot \mathbf{D}_f \\ & + \left[\frac{\partial \Lambda_s}{\partial \vartheta_s} + \rho_s \left(\frac{\eta_s}{\vartheta_s} - \frac{\Lambda_s}{\rho_s \vartheta_s} \right) \right] \dot{\vartheta}_s + \left[\frac{\partial \Lambda_f}{\partial \vartheta_f} + \rho_f \left(\frac{\eta_f}{\vartheta_f} - \frac{\Lambda_f}{\rho_f \vartheta_f} \right) \right] \dot{\vartheta}_f \\ & + \frac{\partial \Lambda_s}{\partial \mathbf{s}_s} \cdot \dot{\mathbf{s}}_s + \frac{\partial \Lambda_f}{\partial \mathbf{D}_f} \cdot \dot{\mathbf{D}}_f + \frac{\partial \Lambda_f}{\partial \mathbf{s}_f} \cdot \dot{\mathbf{s}}_f \geq 0 \end{aligned} \quad (48)$$

If (47) and (48) hold for all processes, then (46) holds for all processes.

Hypothetical processes exist in which all but one of $\mathbf{L}_s, \mathbf{D}_f, \vartheta_s, \vartheta_f, \mathbf{s}_s, \mathbf{D}_f$ and $\dot{\mathbf{s}}_f$ are zero. Therefore, every term in inequality (48) must be separately non-negative. (The same cannot be said of the terms that were segregated into (47).) Furthermore, in the first such separate inequality read off from (48),

$$\left[\frac{\partial \Lambda_s}{\partial \mathbf{F}_s} \mathbf{F}_s^T + \left(\Lambda_s - \frac{\partial \Lambda_s}{\partial \rho_s} \rho_s \right) \mathbf{I} + \vartheta_s \mathbf{T}_s \right] \cdot \mathbf{L}_s \geq 0, \quad (49)$$

the quantity in brackets by assumption does not depend on \mathbf{L}_s . Thus inequality (49) can only be true for all \mathbf{L}_s if the bracketed quantity is zero, that is, if

$$\mathbf{T}_s = -\frac{1}{\vartheta_s} \left[\frac{\partial \Lambda_s}{\partial \mathbf{F}_s} \mathbf{F}_s^T + \left(\Lambda_s - \frac{\partial \Lambda_s}{\partial \rho_s} \rho_s \right) \mathbf{I} \right]. \quad (50)$$

By similar reasoning,

$$\eta_a = \frac{\Lambda_a}{\rho_a} - \frac{\vartheta_a}{\rho_a} \frac{\partial \Lambda_a}{\partial \vartheta_a} \quad (51)$$

$$\frac{\partial \Lambda_a}{\partial \mathbf{s}_a} = \mathbf{0} \quad (52)$$

$$\frac{\partial \Lambda_f}{\partial \mathbf{D}_f} = \mathbf{0}. \quad (53)$$

Moreover, changing the independent variable in (50) from \mathbf{F}_s to $\mathbf{C}_s \equiv \mathbf{F}_s^T \mathbf{F}_s$,

$$\begin{aligned} \mathbf{T}_s &= -\frac{1}{\vartheta_s} \left[\frac{\partial \Lambda_s}{\partial \mathbf{C}_s} \frac{\partial \mathbf{C}_s}{\partial \mathbf{F}_s^T} + \left(\Lambda_s - \frac{\partial \Lambda_s}{\partial \rho_s} \rho_s \right) \mathbf{I} \right] \\ &= -\frac{1}{\vartheta_s} \left[\mathbf{F}_s \left(\frac{\partial \Lambda_s}{\partial \mathbf{C}_s} + \frac{\partial \Lambda_s}{\partial \mathbf{C}_s^T} \right) \mathbf{F}_s^T + \left(\Lambda_s - \frac{\partial \Lambda_s}{\partial \rho_s} \rho_s \right) \mathbf{I} \right]. \end{aligned} \quad (54)$$

One inequality contained in (48) cannot be reduced. In

$$\left[\left(\Lambda_f - \frac{\partial \Lambda_f}{\partial \rho_f} \rho_f \right) \mathbf{I} + \vartheta_f \mathbf{T}_f \right] \cdot \mathbf{D}_f \geq 0, \quad (55)$$

the quantity in brackets depends by assumption on \mathbf{D}_f , so it does not follow that the bracketed quantity must be zero. Results (49)–(55) are similar to standard conclusions for single-phase media.

With the relation (51), the entropy forms of the energy Eqs. (38) and (39) can be written

$$-\frac{\partial \Lambda_s}{\partial \vartheta_s} - \frac{\partial \Lambda_s}{\partial \vartheta_s} \operatorname{div} \mathbf{v}_s = \mathbf{T}_s \cdot \mathbf{L}_s - \operatorname{div} \mathbf{q}_s + \rho_s r_s + z + \frac{\mathbf{w} \cdot \mathbf{f}}{2} \quad (56)$$

$$-\frac{\partial \Lambda_f}{\partial \vartheta_f} - \frac{\partial \Lambda_f}{\partial \vartheta_f} \operatorname{div} \mathbf{v}_f = \mathbf{T}_f \cdot \mathbf{L}_f - \operatorname{div} \mathbf{q}_f + \rho_f r_f - z + \frac{\mathbf{w} \cdot \mathbf{f}}{2}, \quad (57)$$

where definition (40) and the mass balances (15), (16) have been used.

We now turn our attention to inequality (47). It is helpful, but not essential, to break this inequality into several simpler inequalities. Requiring

$$z(\vartheta_s - \vartheta_f) \geq 0 \quad (58)$$

means interphase heat transfer is only allowed to occur from the hotter phase to the colder phase (recall that the coldness ϑ is the reciprocal of the temperature.) Similarly, because absolute temperatures are non-negative, the assertion

$$\frac{\vartheta_s + \vartheta_f}{2} \mathbf{w} \cdot \mathbf{f} \geq 0 \quad (59)$$

means the angle between the interphase force and the excess velocity cannot be larger than a right angle; that is, it is a drag force.

The most common choice for a heat flux constitutive equation is Fourier conduction. This type of heat flux results in each of $\mathbf{q}_s \cdot \mathbf{s}_s$ and $\mathbf{q}_f \cdot \mathbf{s}_f$ being non-negative given a proper choice of material constants.

Left over is a dissipation inequality involving the interphase mass transfer, the fluid volume fraction and the auxiliary internal variables:

$$\left(\frac{\partial \Lambda_s}{\partial \rho_s} - \frac{\partial \Lambda_f}{\partial \rho_f} \right) \hat{\rho} + \frac{\partial \Lambda_s}{\partial \zeta} \dot{\zeta} + \frac{\partial \Lambda_s}{\partial \boldsymbol{\alpha}} \dot{\boldsymbol{\alpha}} + \frac{\partial \Lambda_f}{\partial \zeta} \dot{\zeta} + \frac{\partial \Lambda_f}{\partial \boldsymbol{\alpha}} \dot{\boldsymbol{\alpha}} \geq 0. \quad (60)$$

Requiring (58)–(60) to be satisfied individually is more restrictive than only demanding (47). For instance, (58) asserts that heat can never flow from the colder phase to the hotter phase, no matter how much heat is supplied by the r terms in (38) and (39). The single inequality (47) can be enforced by considering certain equilibrium states, but we do not pursue this here.

The exact form of (41) and the procedure by which we have drawn conclusions from it are obviously crucial. Different entropy axioms and approaches have been proposed by other researchers, notably Krishnaswamy and Batra (1997). In some instances these have been shown to lead to conclusions identical to those from the older Coleman–Noll approach (Klisch, 2002).

5.5. Internal state variable evolution

Internal state variables evolve according to equations other than the balance laws. Generic forms for the fluid volume fraction and the auxiliary internal variables are

$$\dot{\zeta} = \dot{\zeta}(\mathbf{F}_s, \rho_s, \vartheta_s, \mathbf{s}_s, \rho_f, \mathbf{L}_f, \vartheta_f, \mathbf{s}_f, \zeta, \boldsymbol{\alpha}) \quad (61)$$

$$\dot{\boldsymbol{\alpha}} = \dot{\boldsymbol{\alpha}}(\mathbf{F}_s, \rho_s, \vartheta_s, \mathbf{s}_s, \rho_f, \mathbf{L}_f, \vartheta_f, \mathbf{s}_f, \zeta, \boldsymbol{\alpha}) \quad (62)$$

The quantities $\dot{\zeta}$, $\dot{\boldsymbol{\alpha}}$ and $\dot{\boldsymbol{\alpha}}$ can then be obtained from identities (10) and (11) as needed.

5.6. Closure

The preceding development contains many assumptions that taken as a whole define a class of mixed solid–fluid materials we will refer to as standard vascular materials (SVMs). Despite the assumptions made, the class of SVMs allows for very general behavior. It is intended that specific SVMs in this class be useful representations of many types of real vascular materials.

6. Material behavior in simple tension

As we do not wish to develop any computational methods here, we study a very simple SVM undergoing a very simple process: isothermal, uniaxial extension. We calculate the stresses developed in the material due to a prescribed stretch.

6.1. Interphase mass transfer and compressibility

Consider a material composed of a rubbery solid containing finely dispersed, unconnected fluid-filled vesicles. Fluid in the vesicles may solidify and increase the partial density of the solid, reducing the solid partial stress; that is, healing or remodeling the material. Self-healing materials are envisioned to begin healing in response to damage that would otherwise be irreversible. However, for simplicity, healing proceeds here according to a rate equation unconnected to damage. We further assume that Λ_s and Λ_f do not depend on the fluid volume fraction ζ . Therefore, no internal state variables are needed.

Under these assumptions, the dissipation inequality (60) simplifies to

$$\left(\frac{\partial \Lambda_s}{\partial \rho_s} - \frac{\partial \Lambda_f}{\partial \rho_f} \right) \hat{\rho} \geq 0. \quad (63)$$

A similar inequality appears in Ambrosi et al. (2010), which considered mixtures in which the constituents have the same temperature. The quantity $\partial \Lambda_s / \partial \rho_s - \partial \Lambda_f / \partial \rho_f$ may be interpreted as a driving force for the conversion of fluid to solid. It may be anticipated that some part of Λ_a chosen for a particular material must contain a term that directly governs the rate of fluid–solid conversion, but the appearance of $\partial \Lambda_a / \partial \rho_a$ means other terms in Λ_a involving ρ_a must play a role as well. A constitutive equation of the form

$$\hat{\rho} = f(\mathbf{w}, \rho_s, \rho_f) \left(\frac{\partial \Lambda_s}{\partial \rho_s} - \frac{\partial \Lambda_f}{\partial \rho_f} \right), \quad (64)$$

where $f \geq 0$, ensures the interphase mass transfer will satisfy the entropy axiom. Eq. (64) is certainly not the only form that satisfies the entropy axiom, but it is the most obvious. If it is adopted, the direction of interphase mass transfer depends on the sign of $\partial \Lambda_s / \partial \rho_s - \partial \Lambda_f / \partial \rho_f$.

By definition, an incompressible material is one in which the density cannot change. For conventional materials, density changes can only be brought about by deformation; therefore, incompressibility can be enforced solely by constraining the deformation. The phases in the SVM differ from conventional materials in that both deformation and interphase mass transfer can cause phase density changes. Therefore, assuming a phase to be incompressible would place a coupled constraint on both the deformation and the interphase mass transfer. We do not wish to

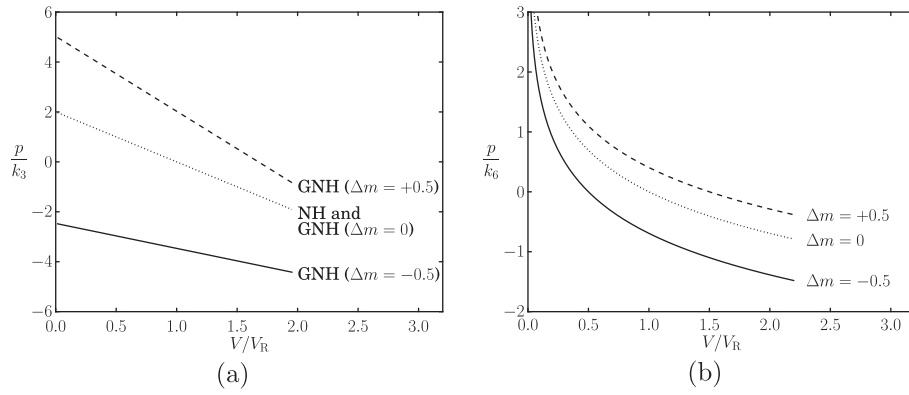


Fig. 2. Bulk behavior of the solid phase (a) and fluid phase (b). For the solid phase, $k_8 = 5k_3$, NH denotes the classical Neo-Hookean model and GNH denotes the generalized Neo-Hookean model (69).

examine the implications of such a constraint at this time. Also, intrinsic incompressibility can only be enforced when the fluid volume fraction is tracked. Therefore, both phases will be assumed compressible.

A mechanically compressible fluid usually means a gas, which would imply that its intrinsic density should also be changed by temperature. But for simplicity, the fluid in the present example is intended to be a liquid and has no thermal expansion. As stated above, the fluid is allowed to be intrinsically compressible only to avoid developing a complicated constraint that would distract from the main development. The fluid bulk modulus in this example can be arbitrarily high, just not infinite.

6.2. Stress constitutive equations

The ideal mixture assumption allows us to leverage certain results from the study of single-phase continua. When the solid phase is isotropic, it is well known that the dependence of Λ_s on \mathbf{F}_s can only be through the invariants of \mathbf{C}_s . Let the principal scalar invariants of \mathbf{C}_s be I_1, I_2 and I_3 . Assuming $\Lambda_s(\mathbf{C}_s) = \Lambda_s(\mathbf{C}_s^T)$, from Eq. (54) we have

$$\mathbf{T}_s = \beta_0 \mathbf{I} + \beta_1 \mathbf{B}_s + \beta_{-1} \mathbf{B}_s^{-1}, \quad (65)$$

where $\mathbf{B}_s \equiv \mathbf{F}_s \mathbf{F}_s^T$ and

$$\begin{aligned} \beta_0 &\equiv \frac{\rho_s}{\rho_{sR}} \left(2I_3 \frac{\partial U}{\partial I_3} + 2I_2 \frac{\partial U}{\partial I_2} - \rho_s \frac{\partial U}{\partial \rho_s} \right) & \beta_1 &\equiv 2 \frac{\rho_s}{\rho_{sR}} \frac{\partial U}{\partial I_1} \\ \beta_{-1} &\equiv -2 \frac{\rho_s}{\rho_{sR}} I_3 \frac{\partial U}{\partial I_2}. \end{aligned} \quad (66)$$

In the above equations, ρ_{sR} is the solid density in the reference configuration. These equations are the same as those from finite elasticity theory except that, due to interphase mass transfer, we cannot assume $\rho_s = \rho_{sR} I_3^{-1/2}$.

The energy balance and entropy axiom were developed in terms of Λ_s , the Massieu potential per unit present volume, which is related to the strain energy per unit reference volume by

$$\Lambda_s = -\rho_s U \vartheta_s / \rho_{sR}. \quad (67)$$

The solid Massieu potential

$$\Lambda_s = -\frac{\vartheta_s \rho_s}{\rho_{sR}} \left[k_2 (I_3^{-1/3} I_1 - 3) + k_3 (I_3^{1/3} - 1)^2 \right] + k_8 \vartheta_s \ln \left(\frac{\rho_s}{\rho_{sR}} I_3^{1/2} \right) \quad (68)$$

results, by (67), in a generalized compressible Neo-Hookean strain energy function

$$U = k_2 \left(I_3^{-1/3} I_1 - 3 \right) + k_3 \left(I_3^{1/3} - 1 \right)^2 - k_8 \frac{\rho_{sR}}{\rho_s} \ln \left(\frac{\rho_s}{\rho_{sR}} I_3^{1/2} \right). \quad (69)$$

This equation reduces to the classical compressible Neo-Hookean strain energy function when there is no interphase mass transfer; that is, when $\rho_s = \rho_{sR} I_3^{-1/2}$. In this simple example, the solid has no thermal expansion or other coupling between deformation and temperature. A complete absence of material causes a singularity in this form, as well as other breakdowns in the theory, so we exclude $\rho_s = 0$ and $\rho_f = 0$ *a priori*.

From (65), (66) and (69),

$$\begin{aligned} \mathbf{T}_s = & \left[2k_3 \frac{\rho_s}{\rho_{sR}} \left(I_3 - I_3^{1/3} \right) - \frac{2}{3} k_2 \frac{\rho_s}{\rho_{sR}} I_1 I_3^{-1/3} - k_8 \ln \left(\frac{\rho_s}{\rho_{sR}} I_3^{1/2} \right) \right] \mathbf{I} \\ & + 2k_2 \frac{\rho_s}{\rho_{sR}} I_3^{-1/3} \mathbf{B}_s. \end{aligned} \quad (70)$$

The solid strain energy and stress vanish in the reference configuration, but interphase mass transfer or deformation or both cause nonzero stress in other configurations. Interphase mass transfer by itself changes the stress in any given deformed configuration.

Eq. (70) implies that a pure dilatation in which the volume of the solid changes from a reference value of V_R to a final value of V requires a hydrostatic pressure

$$p = 2k_3 \frac{\rho_s}{\rho_{sR}} \left(\frac{V}{V_R} - \frac{V^2}{V_R^2} \right) + k_8 \ln \frac{\rho_s V}{\rho_{sR} V_R}. \quad (71)$$

This hydrostatic response is illustrated in Fig. 2(a) for several assumed changes in the mass of the solid phase. Because density is a function of mass and volume, the relationship between pressure and volume turns out to be linear. This cannot hold true generally, otherwise the body could be compressed out of existence with a finite pressure. The bulk response predicted by (70) should be viewed as a linear approximation valid for small changes in volume.

The generalized model just described is a simple extension of the Neo-Hookean model used for single-phase compressible elastic materials. Comparison to experiment will be necessary to determine whether it describes any real materials well. Development of constitutive equations for any particular real material is outside of the scope of this paper.

The fluid is assumed to be Newtonian and compressible. By standard arguments exploiting requirement (55), the stress in the fluid is

$$\mathbf{T}_f = (k_4 \text{tr} \mathbf{D}_f - p_f) \mathbf{I} + 2k_5 \mathbf{D}_f, \quad (72)$$

where

$$p_f = \frac{1}{\vartheta_f} \left(\Lambda_f - \rho_f \frac{\partial \Lambda_f}{\partial \rho_f} \right) \quad (73)$$

is the thermodynamic pressure and $k_4 \text{tr} \mathbf{D}_f$ is the viscous pressure.

We propose a fluid Massieu potential

$$\Lambda_f = k_6 \vartheta_f \left(\ln \frac{\rho_f}{\rho_{fr}} + 1 \right), \quad (74)$$

where ρ_{fr} is the density of the fluid in the reference configuration. With (74),

$$\mathbf{T}_f = \left[k_4 \text{tr} \mathbf{D}_f - k_6 \ln \frac{\rho_f}{\rho_{fr}} \right] \mathbf{I} + 2k_5 \mathbf{D}_f. \quad (75)$$

Eq. (75) shows that the fluid stress is zero when at rest in the reference configuration, but a density change brought about solely by interphase mass transfer will cause a change in pressure.

For a static deformation, $\mathbf{D} = \mathbf{0}$ and the fluid stress consists only of the negative of the thermodynamic pressure. The bulk modulus is defined as $B \equiv -V \partial p / \partial V$, which for a constant mass of fluid is just k_6 . Thus, k_6 is the “mechanical” bulk modulus of the fluid, meaning the value when there is no interphase mass transfer. The fluid pressure–volume relationship is illustrated in Fig. 2(b) for several assumed changes in the mass of the fluid phase.

Both the solid and fluid stress are functions of the ratios ρ_a / ρ_{ar} . In the momentum balances, when the divergence of stress is taken, spatial derivatives of both ρ_a and ρ_{ar} will generally appear. For simplicity, we will assume in this application that the ρ_{ar} are spatially uniform, so that their spatial derivatives vanish. However, the stress is zero everywhere in the reference configuration whether or not the reference densities are spatially uniform.

Using (68) and (74) in (64), a form of the interphase mass transfer constitutive equation that ensures satisfaction of the entropy axiom is

$$\hat{\rho} = f(\mathbf{w}, \rho_f, \rho_s) \left[\frac{k_8 \vartheta_s}{\rho_s} - \frac{k_2 \vartheta_s}{\rho_{sr}} \left(I_3^{-\frac{1}{3}} I_1 - 3 \right) - \frac{k_3 \vartheta_s}{\rho_{sr}} \left(I_3^{\frac{1}{3}} - 1 \right)^2 - \frac{k_6 \vartheta_f}{\rho_f} \right] \quad (76)$$

where $f(\mathbf{w}, \rho_f, \rho_s)$ is never negative, but zero if $\mathbf{w} \neq \mathbf{0}$, in order to satisfy (25). One way to satisfy this requirement is to set $f(\mathbf{w}, \rho_f, \rho_s) = k_1 \exp(-k_7 \mathbf{w} \cdot \mathbf{w})$, where $k_1 \geq 0$ and k_7 may be chosen large, so that $\hat{\rho}$ practically vanishes when \mathbf{w} is much different from $\mathbf{0}$.

When there is no relative motion of the fluid and solid ($\mathbf{w} = \mathbf{0}$) and no temperature difference ($\vartheta_s = \vartheta_f \equiv \vartheta$), the interphase mass transfer may be simplified to

$$\hat{\rho} = \tilde{k}_1 \left[\frac{k_8}{\rho_s} - \frac{k_2}{\rho_{sr}} \left(I_3^{-\frac{1}{3}} I_1 - 3 \right) - \frac{k_3}{\rho_{sr}} \left(I_3^{\frac{1}{3}} - 1 \right)^2 - \frac{k_6}{\rho_f} \right] \quad (77)$$

where $\tilde{k}_1 \equiv k_1 \vartheta$.

Insight may be gained into this constitutive equation for interphase mass transfer by considering its behavior for a dilatation such that all stretches are λ . Then $I_1 = 3\lambda^2$, $I_3 = \lambda^6$, and

$$\hat{\rho} = \tilde{k}_1 \left[\frac{k_8}{\rho_s} - \frac{k_3}{\rho_{sr}} (\lambda^3 - 1)^2 - \frac{k_6}{\rho_f} \right]. \quad (78)$$

Thus, fluid may solidify ($\hat{\rho} > 0$) or solid may liquefy ($\hat{\rho} < 0$), depending on the values of k_3 , k_6 and k_8 , the magnitude of the dilatation and the partial densities. For real materials, the physical interpretations of k_3 and k_6 are clear and their values are normally positive, and k_8 can be interpreted as an additional bulk response coefficient that should also be positive. If we had used a classical Neo-Hookean model for the solid, the k_8 term would not have appeared, the quantity in brackets could never be positive, and fluid could never solidify.

Supposing k_6 and k_8 to be positive, an increase in ρ_s would slow down the rate of conversion of fluid to solid, while an increase in ρ_f would speed it up. If solidification is a chemical process, such as the curing of an epoxy, this is consistent with the chemical law

of mass action, which states that a reaction proceeds more quickly when more of the reactants are present.

6.3. Interphase force

In this example, relative solid–fluid motion is prevented by a constraint response that is assumed to produce no entropy in any motion compatible with the constraint. We write the interphase force as $\mathbf{f} = \mathbf{g} + \mathbf{h}$, where \mathbf{g} is determined by a constitutive equation and \mathbf{h} maintains the constraint. Often, some insight can be gained into the form of the constraint response by exploiting the requirement of worklessness, but the work done by \mathbf{h} is $\mathbf{w} \cdot \mathbf{h}$, which is zero for any process compatible with the constraint $\mathbf{w} = \mathbf{0}$ regardless of the form of \mathbf{h} and therefore places no restriction on the form of \mathbf{h} . Since the constraint response adds an arbitrary non-constitutive vector to \mathbf{f} , the entire value \mathbf{f} may be regarded as non-constitutive without loss of generality. The overall effect of the constraint $\mathbf{w} = \mathbf{0}$ is to replace one of the phase velocities by the constraint response.

The SVM just described is very simple, with no thermal effects, internal state variables or even relative solid–fluid motion. Seven constants are required to characterize the material, and not all of those constants may have significant influence in every application. This is manageable from an engineering viewpoint.

6.4. Problem formulation

We study the stress response to a prescribed, time-dependent stretch in the 1-direction. The momentum balances are satisfied identically. The stress field only needs to satisfy the lateral boundary condition $T_{22} = 0$, $T_{33} = 0$. This condition will be used to solve for the lateral stretch, which will then enable calculation of the traction T_{11} that results from the prescribed axial stretch.

The mass balances are

$$\rho'_s + \rho_s \left(\frac{\lambda'_1}{\lambda_1} + 2 \frac{\lambda'_2}{\lambda_2} \right) = \tilde{k}_1 \left[\frac{k_8}{\rho_s} - \frac{k_2}{\rho_{sr}} \left(I_3^{-\frac{1}{3}} I_1 - 3 \right) - \frac{k_3}{\rho_{sr}} \left(I_3^{\frac{1}{3}} - 1 \right)^2 - \frac{k_6}{\rho_f} \right] \quad (79)$$

$$\rho'_f + \rho_f \left(\frac{\lambda'_1}{\lambda_1} + 2 \frac{\lambda'_2}{\lambda_2} \right) = -\tilde{k}_1 \left[\frac{k_8}{\rho_s} - \frac{k_2}{\rho_{sr}} \left(I_3^{-\frac{1}{3}} I_1 - 3 \right) - \frac{k_3}{\rho_{sr}} \left(I_3^{\frac{1}{3}} - 1 \right)^2 - \frac{k_6}{\rho_f} \right] \quad (80)$$

and the condition of zero lateral stress is

$$\begin{aligned} 2 \frac{\rho_s}{\rho_{sr}} \left[k_3 \left(I_3 - I_3^{\frac{1}{3}} \right) - \frac{k_2}{3} I_1 I_3^{-\frac{1}{3}} \right] + 2k_2 \frac{\rho_s}{\rho_{sr}} I_3^{-\frac{1}{3}} \lambda_2^2 + k_4 \left(\frac{\lambda'_1}{\lambda_1} + 2 \frac{\lambda'_2}{\lambda_2} \right) \\ - k_6 \ln \frac{\rho_f}{\rho_{fr}} + k_8 \ln \left(\frac{\rho_s}{\rho_{sr}} I_3^{\frac{1}{3}} \right) + 2k_5 \frac{\lambda'_2}{\lambda_2} \\ = 0. \end{aligned} \quad (81)$$

With $\lambda_1(t)$ prescribed, these are three ordinary differential equations governing ρ_s , ρ_f and λ_2 .

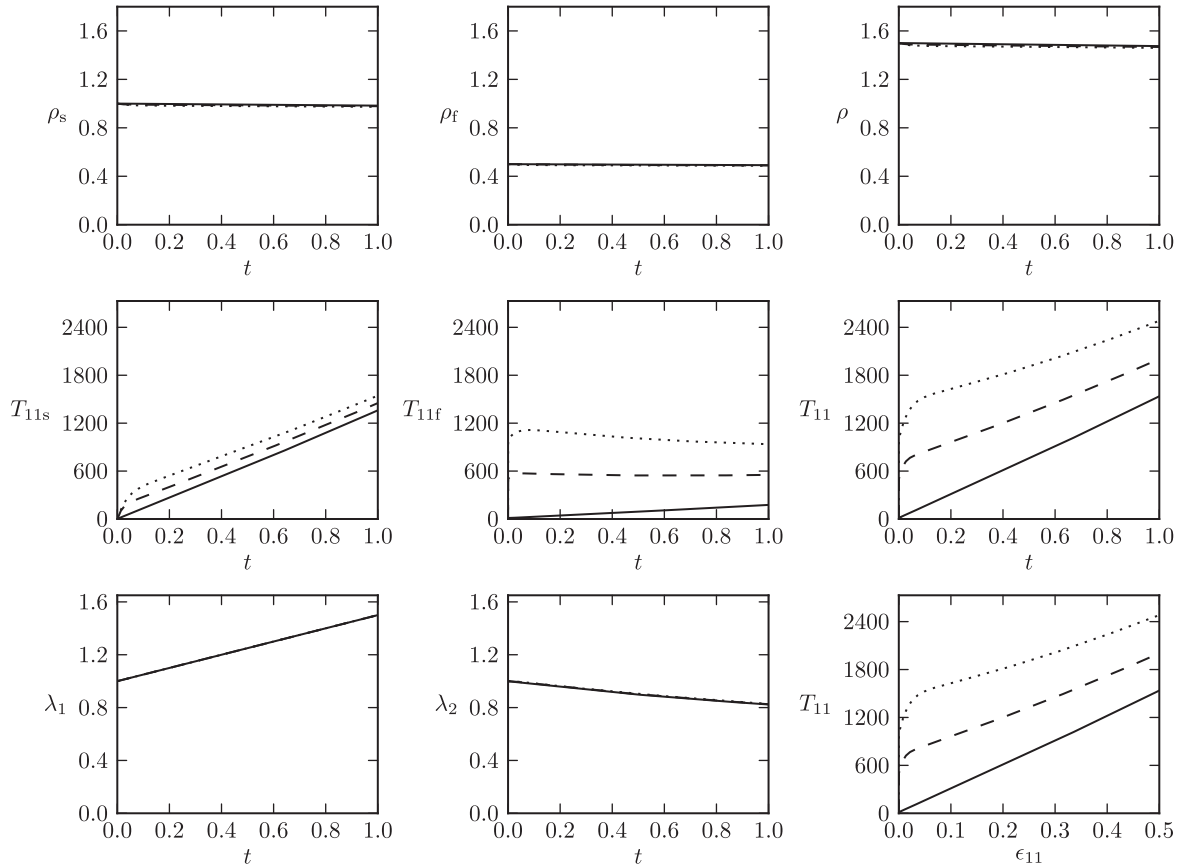
6.5. Simulation results

Eqs. (79)–(81) comprise a set of differential–algebraic equations easily solved by finite differencing. This was implemented with the open-source mathematics software *sage* (Stein et al., 2011), and the plots were generated using *matplotlib* (Hunter, 2007). Table 1 lists the material parameters, their dimensions and physical interpretations, and a baseline set of values. From here on, only departures from the baseline are mentioned.

Each set of results is shown as a group of nine plots. The top three are the solid, fluid and material density versus time; the middle three are solid, fluid and material axial stress versus time; and the first two in the bottom row are the (prescribed) axial and (resulting) lateral stretches versus time. The final plot, in the lower right-hand corner of each group, is axial stress versus axial strain.

Table 1Material parameters and physical interpretations. M denotes mass, L length, t time and θ temperature.

Parameter	Interpretation	Baseline value	Dimensions
ρ_{sR}	Reference density of the solid phase	1.0	M/L ³
ρ_{fR}	Reference density of the fluid phase	0.5	M/L ³
\bar{k}_1	Interphase mass transfer constant	0	Mt/L ⁵ θ
k_2	Half the initial shear modulus of the solid phase	5×10^2	F/L ²
k_3	First partial bulk modulus of the solid phase	10^4	F/L ²
k_4	Bulk viscosity of the fluid phase	1	Ft/L ²
k_5	Shear viscosity of the fluid phase	10^3	Ft/L ²
k_6	Bulk modulus of the fluid phase	10^4	F/L ²
k_8	Second partial bulk modulus of the solid phase	10^4	F/L ²

**Fig. 3.** Material tensile response for $k_5 = 10$ (solid curve), 500 (dashed), 1000 (dotted).

In the first two sets of simulations, it is simply a conventional stress–strain curve. In the third and fourth sets of simulations, the stretch rate is not constant, but stress versus strain over the entire time of the simulation is included for completeness.

We first consider the effect of varying k_5 , the shear viscosity of the fluid, when the tensile specimen is subjected to the stretch history

$$\lambda_1 = 1 + at, \quad 0 \leq t \leq 1. \quad (82)$$

Fig. 3, in which $a = 0.5$, shows that the material is nearly incompressible with the baseline choice of constants. Increasing k_5 causes the fluid partial stress to increase, as would be expected, but also causes a slight increase in the solid partial stress. The total stress increases as k_5 increases. The response is nonlinear, especially at the smaller stretch values. Because the stretch rate is nonzero and constant for $t > 0$, stress develops in the fluid immediately, whereas stress only develops in the solid as stretch accumulates.

Fig. 4 shows the response to the same axial stretch history for three increasing values of the solid initial shear modulus k_2 . As

would be expected, the stress in the solid increases accordingly, whereas the stress in the fluid is unaffected. Further studies, not illustrated here, showed that the response was practically unaffected by changes in either of the solid bulk modulus parameters k_3 and k_8 .

Fig. 5 shows the effect of different stretch rates a on a material of fixed baseline composition. As one would expect, the apparent modulus of the material increases as the stretch rate increases.

Fig. 6 shows the response of a specimen stretched at constant rate of 0.5 and then held at 125% stretch, as in a stress relaxation test:

$$\lambda_1 = \begin{cases} 1 + 0.5t & 0 \leq t \leq 0.5 \\ 1.25 & 0.5 < t \leq 1.0 \end{cases} \quad (83)$$

In these simulations the fluid shear modulus k_5 is increased to 5×10^3 in order to amplify the rate dependence originating in the fluid. The fluid bulk modulus k_6 takes on the values 10, 10^4 and 10^5 .

Figs. 5 and 6 show that an SVM can exhibit rate dependence of the tensile modulus, as well as both instantaneous and

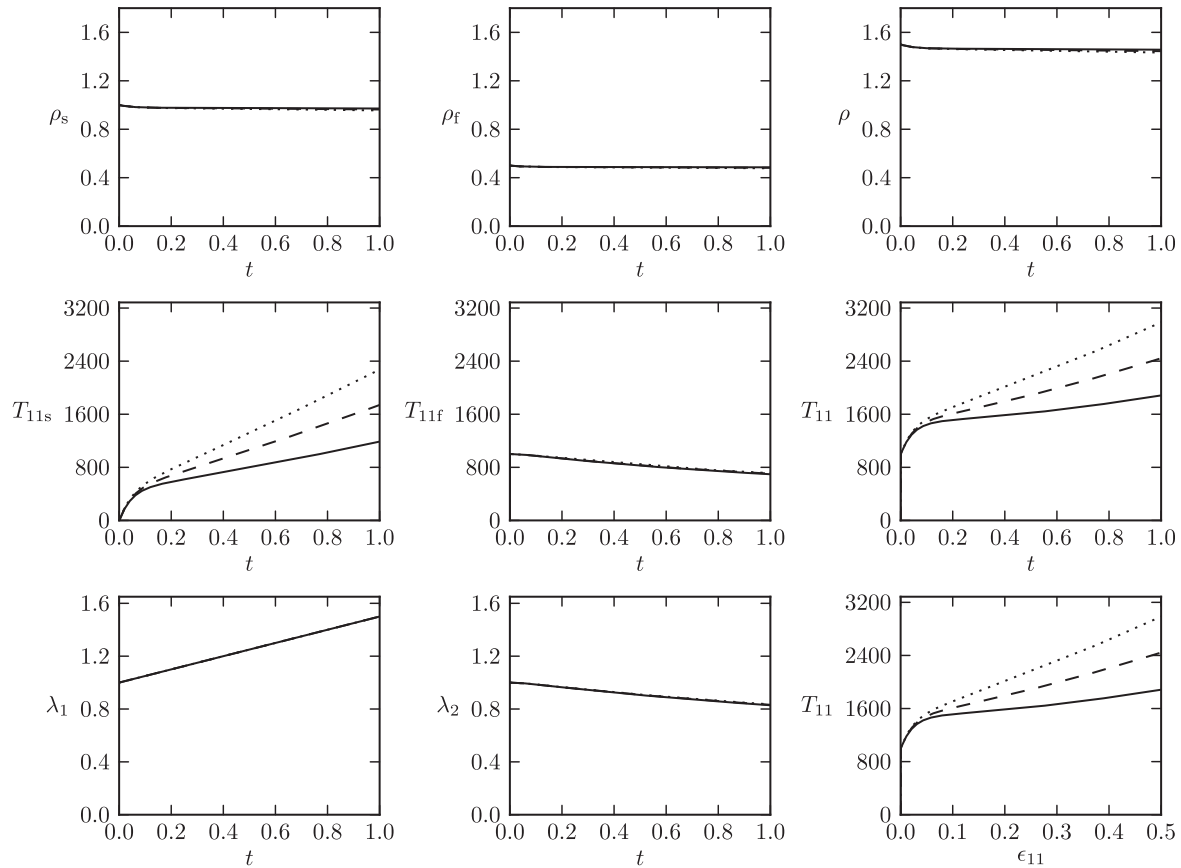


Fig. 4. Material tensile response for $k_2 = 300$ (solid curve), 500 (dashed), 700 (dotted).

long-term stress relaxation, even without including viscoelastic phases. The relaxation and rate-dependent stiffness of this material would allow it to provide damping and tailored or controllable stiffness.

Up to this point the simulations have shown fairly conventional time- and rate-dependent material response. Now, we introduce interphase mass transfer by allowing \bar{k}_1 to take on nonzero values.

A body's volume increases when it is subjected to simple tension, and the phase partial densities therefore naturally decrease in the absence of interphase mass transfer. If the fluid can undergo solidification during the stretching process, three regimes of behavior may be identified: (i) solidification at a rate insufficient to offset the solid density decrease due to deformation alone, (ii) solidification at a rate that just balances the natural solid density decrease or (iii) solidification at a rate sufficient to overcome the natural solid density decrease, so that the density of the solid actually increases during the stretching process. The fluid density decreases no matter what.

Referring to Eq. (77), fluid will solidify (thus providing healing) only if k_8 is large compared to k_6 and k_3 . Fig. 7 shows the tensile response of a material for $k_6 = 5 \times 10^3$, $k_8 = 3 \times 10^4$ subjected to the axial stretch history (82) with $a = 0.5$.

Results for three values of \bar{k}_1 are shown. For the first value, $\bar{k}_1 = 0$, the material is in regime (i). Solidification is too slow to prevent a decrease in the solid density as the specimen is stretched. The solid and fluid each bear a similar fraction of the total stress. For the second value, $\bar{k}_1 = 5 \times 10^{-6}$, the material is close to regime (ii). Solidification is such that the solid density is almost constant, increasing by only 0.4% during the stretching. The solid bears only a small fraction of the total stress because of the healing effect, while the fluid now bears almost all of the stress. For the third value, $\bar{k}_1 = 10 \times 10^{-6}$, solidification is fast enough to reverse the nat-

ural decrease in solid density. The solid actually goes into compression because its density is increasing faster than can be "made room" for it by the stretching deformation. By the end of the stretching, the solid density has increased by 4.5%, while the fluid density has decreased by 41%. Mass is, of course, conserved for the material as a whole, but the material density ρ decreases by 11% due to the deformation.

These results are consistent with an intuitive conception of a healing process. The transfer of fluid to solid reduces the stress in the solid, preventing it from possibly failing. But the material as a whole does not gain in stiffness, because the fluid was already carrying tension before it solidified. A real fluid would cavitate and lose load-carrying capability if the tension became high enough, but such behavior is not modeled in this example.

7. Conclusions

In this paper, a class of idealized standard vascular materials based on continuum mixture theory has been developed. These materials are composed of a solid phase and a fluid phase that may exchange mass, momentum and heat, so that engineering materials with fluid carried through a vascular network in the solid skeleton can be simulated. The fluid can enable much structural versatility, such as healing and remodeling, thermal management and damping. The isothermal uniaxial tension behavior of one member of this class has been simulated, and displays healing, rate-dependent stiffness, and instantaneous and long-term stress relaxation.

Possible directions for further research include numerical implementation of this relatively tractable modeling approach, more complex simulations including thermal effects, relative

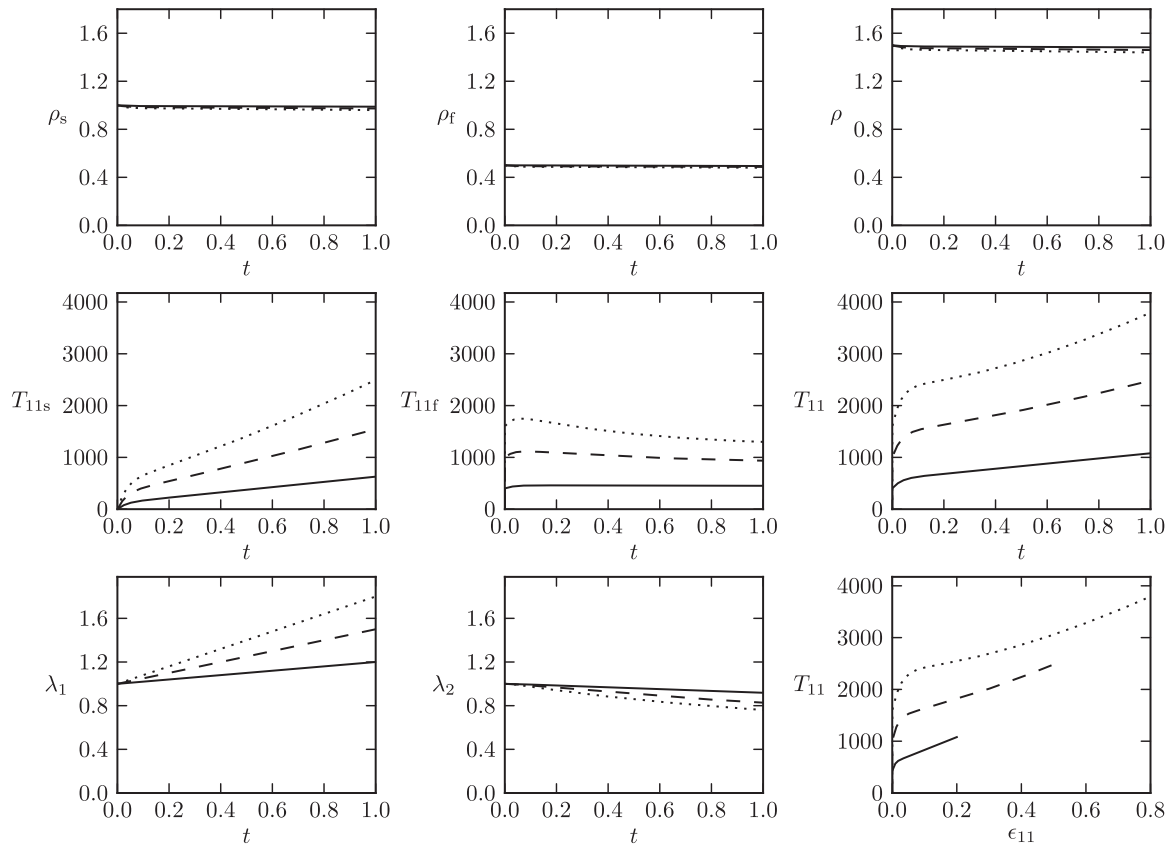


Fig. 5. Response to stretch rates of 0.2 (solid curve), 0.5 (dashed) and 0.8 (dotted).

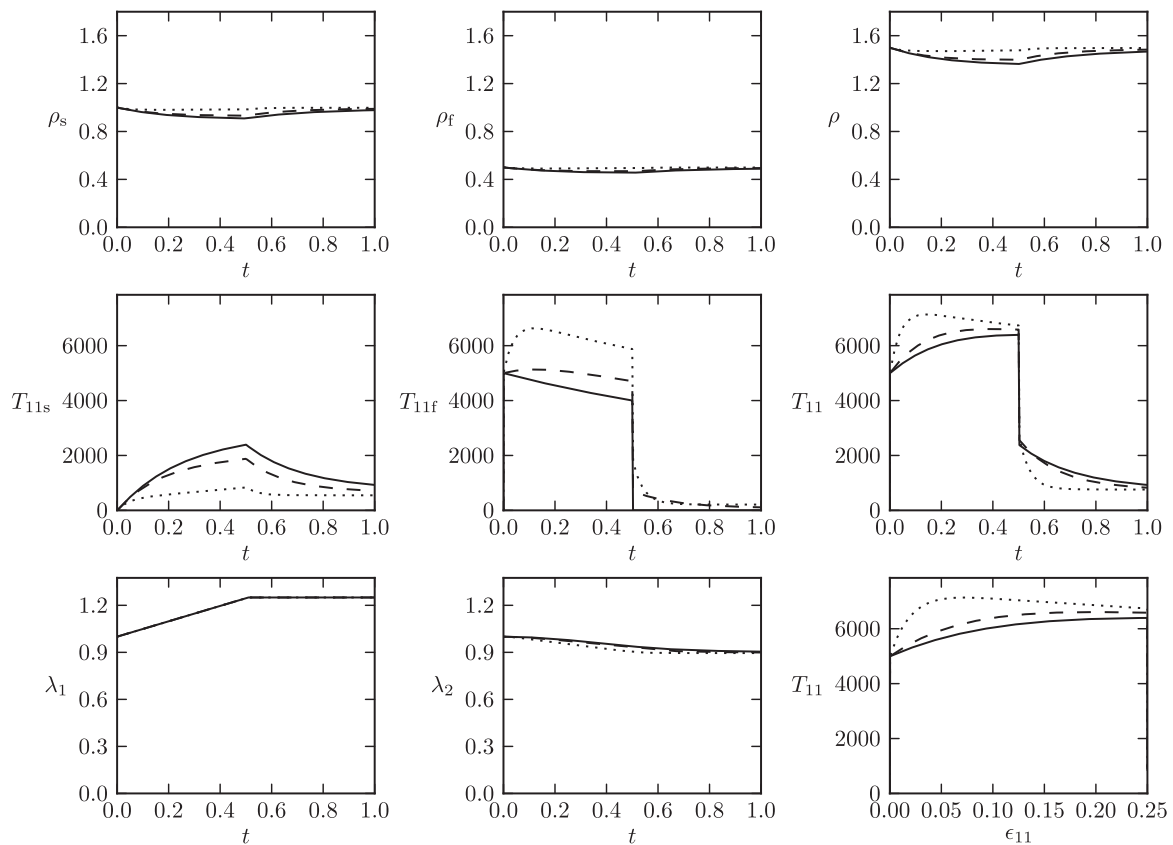


Fig. 6. Response to constant-rate stretch followed by hold for $k_6 = 10$ (solid curve), 10^4 (dashed), 10^5 (dotted). k_5 was increased to 5×10^3 from its baseline value for this set of simulations.

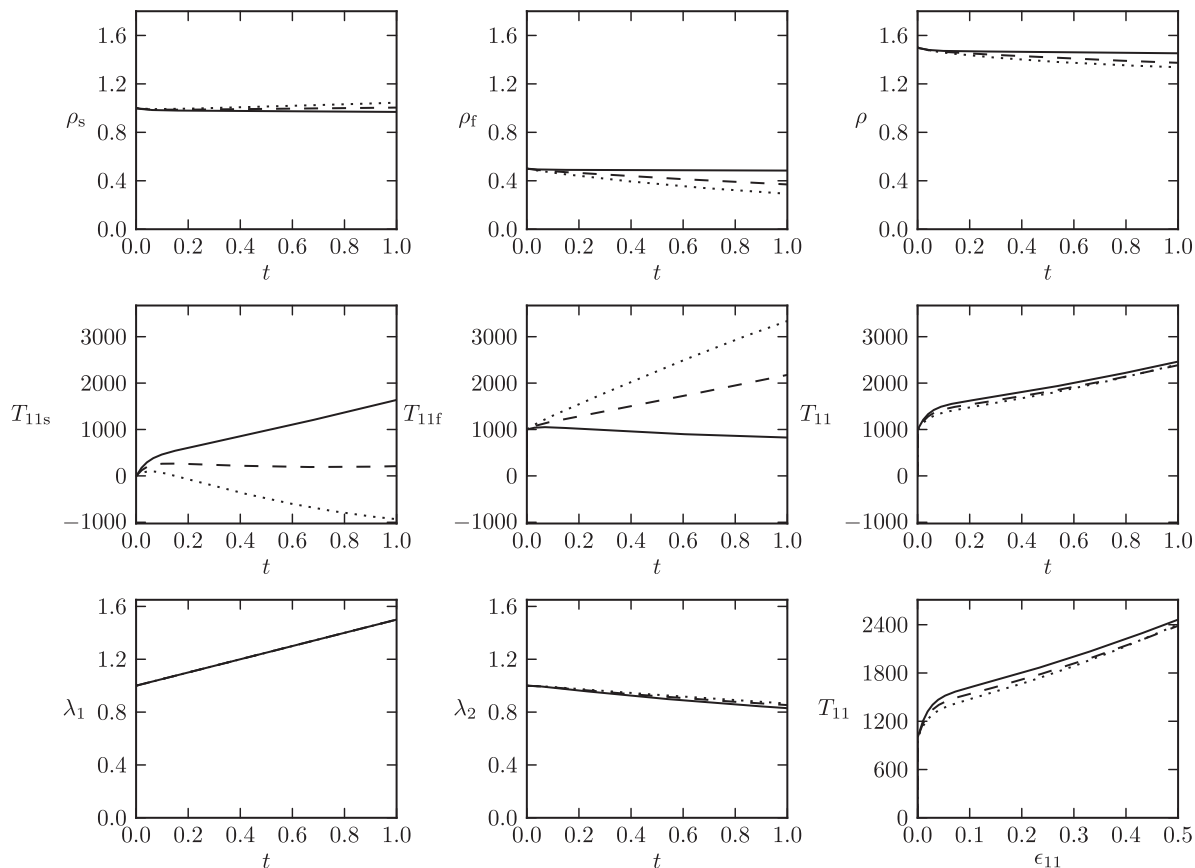


Fig. 7. Material tensile response with no solidification ($k_1 = 0$, solid curve), and solidification at rates governed by $k_1 = 5 \times 10^{-6}$ (dashed) and 10×10^{-6} (dotted).

motion between the solid and fluid, internal variable representations of damage, investigation of the appropriate types of boundary conditions for realistic problems, and use of this approach to design, synthesize and characterize new biphasic fluid–solid materials for high-performance structural applications.

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